

Ferrate(VI): Testable Hypothesis for the Martian Oxidant

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The Viking Gas Chromatograph Mass Spectrometer failed to detect organic matter on Mars, and both the Viking Labeled Release and Gas Exchange experiments indicated a highly oxidizing reactive soil on Mars surface. Here a hypothesis is examined, on the possible involvement of highest oxidation state iron, ferrate(VI), FeO_4^{2-} , as a compound contributing to the oxidizing power of Martian soil. Environmental conditions on Mars appear compatible with ferrate(VI) formation and preservation, and it is shown, that this form of iron oxidizes water with oxygen release, and produces carbon dioxide from various organic materials, such as components of nutritional mixture used in Viking “biological experiments”. These reactions are inhibited by ferrate pre-heating due to its thermal decomposition. Spectral approaches are explored for iron(VI) identification by remote sensing and contact measurements in future Mars missions.

1. INTRODUCTION

The proposed program of Mars exploration for the next decade (Mars Surveyor Program, MSP) includes a number of missions at two year intervals. Already the Mars ‘98 polar missions (orbiter and lander) are on their way, to be followed by missions in ‘01, ‘03, and ‘05, the latter two of which will involve collection of samples from the Martian surface. In all these missions, including the Mars Sample Return (MSR), one will complete some measurements of physical, chemical, and geological properties of Mars, by both *in situ* studies of the surface and the atmosphere, and the analyses of returned samples. Key among the investigations, however, will be the search for life in the Universe, with particular focus on Mars, given its planetary history and its proximity to Earth. Mostly due to the Viking missions in the 1970’s, and more recent Pathfinder investigations, considerable knowledge has been acquired on the geology and chemical

composition of Mars (Banin *et al.*, 1992, McSween *et al.*, 1999). The “biological” experiments on the Viking landers (Oyama *et al.*, 1976, Levin and Straat, 1976) revealed unexpected chemical activity in the surface material, which in some ways resembled biology but was ultimately explained by a complex chemistry. These experiments showed that moisturizing Martian soil resulted in oxygen evolution, while addition of a bacterial nutrient solution (^{14}C -labeled formate, glycine, lactate, alanine, and glycolate) resulted in $^{14}\text{CO}_2$ evolution in the reaction chamber, together with some formation of oxygen. Release of CO_2 was inhibited almost completely after sterilizing the Martian soil sample at 160°C for 3 hours, while O_2 formation was only partially inhibited by such a preheating. These observations were interpreted as indications on the presence of a strong oxidant on Martian surface, or, most probably, several different types of oxidants (Klein 1978, Zent and McKay 1994). Samples of terrestrial soils from locations around the world were used to test Viking equipment. No site on Earth was found with such a strong oxidant present, capable of decomposing water. This is not unexpected taking into account the abundance of reductants that make unlikely the accumulation of such a strong oxidant anywhere on the surface of the Earth.

It's important to understand the nature of Martian oxidant, and its likely distribution pattern. Is this oxidant(s) located only on the surface, or what is its vertical profile in Martian soil? Is it distributed uniformly areas without oxidant at all can be located? What about polar areas? The answers for these questions are of paramount interest for choosing landing sites for MSR, and for the entire program of Mars exploration.

Several candidates were proposed on the role of Martian oxidants: iron oxides (possibly $\gamma\text{-Fe}_2\text{O}_3$), hydrogen peroxide and other active oxygen species, such as superoxide radical ions, which can be formed due to the UV irradiation of Martian soil (Bullock *et al.* 1994, Hunten 1979, Huguenin *et al.*, 1979, Levin and Straat 1981, McDonald *et al.* 1998, Yen 1999).

Recently, it was shown that titanium dioxide adsorbs hydrogen peroxide on its surface, and the resulting system can mock Viking experiments in laboratory conditions fairly well (Quinn and Zent 1999). Titanium dioxide is present in Martian soil indeed (Banin *et al.*, 1992), with its estimated abundance of 0.6 mass %. However, out of the other elements with well established set of variable oxidation states, iron is the most attractive candidate, due to its abundance in Martian soil (third most

abundant element, after oxygen and silicon, about 18 mass % on Fe_2O_3 basis). The very color of the planet is due to iron oxide(s). Therefore, it seems iron deserves more careful attention as potential source of chemical activity of the Martian soil.

Iron typically occurs as a free metal, or in the oxidation states $\text{Fe}(+2)$ or $\text{Fe}(+3)$. However, at certain conditions, higher oxidation states of iron can be formed, as $\text{Fe}(\text{IV})$, $\text{Fe}(\text{V})$, and $\text{Fe}(\text{VI})$ [see, e.g., (Turova 1997)]. Out of these, $\text{Fe}(\text{IV})$ and $\text{Fe}(\text{V})$ are extremely unstable, and decompose (dismutate) into $\text{Fe}(\text{III})$ and $\text{Fe}(\text{VI})$ under all reasonable conditions imaginable, and will not be considered here. However, $\text{Fe}(\text{VI})$, known in the form of several ferrate(VI) salts, even though an extremely strong oxidant, is a well characterized chemical species. Though it was never found on the Earth, it is stable enough under some conditions that are not met in the terrestrial environment, but still can be considered as a possibility in Martian soil. Formation of ferrate(VI) as a purple by-product in some strongly alkaline solutions, was first described as early as in 1702 (Stahl 1715). More recently, ferrates(VI) with various cations, such as potassium, sodium, barium, lithium, rubidium, cesium, silver(I) and even few tetraalkyl/aryl ammonium salts, have been described (Thompson *et al.* 1951, Delaude and Laszlo 1996, Malchus and Jansen 1998, Kulikov *et al.* 1999). Well characterized potassium ferrate(VI), K_2FeO_4 , has been prepared as dark purple, almost black crystals, decomposing starting ca. 200°C with oxygen release (Thompson *et al.* 1951). Currently, there is a burst of interest to ferrate (VI) as a promising oxidizing reagent for organic synthesis (Delaude and Laszlo 1996, Johnson and Hornstein, 1996) and material for rechargeable alkaline batteries of high capacity (Licht *et al.*, 1999).

Here we present data on ferrate(VI) spectral characterization and chemical activities under the conditions of simulated Viking “biological” experiments.

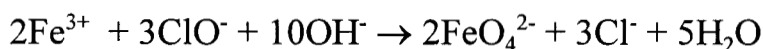
2. EXPERIMENTAL

2.1 Ferrate(VI) Preparation

Several procedures were previously suggested to prepare ferrate(VI): electrochemical oxidation of iron anode (Denvir and Pletcher 1996), calcination of a mixture of ferric oxide with potassium peroxide in the stream of oxygen gas (Dedushenko, *et al.* 1989), and wet oxidation of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{VI})$ by hypochlorite or hypobromite in a highly basic solution

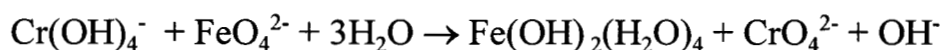
(Thompson *et al.* 1951). The last approach seems most practical for preparation purposes, and was applied in these experiments.

Crystalline potassium ferrate was prepared by the wet procedure, essentially as outlined by Delaude and Laszlo, 1996. First, concentrated solution of potassium hypochlorite, KClO, was formed by bubbling chlorine gas into cold 10 M KOH solution. The potassium chloride by-product precipitated upon addition of an excess of solid KOH and was removed by filtration. Then iron(III) nitrate, Fe(NO₃)₃·12H₂O, was added in small portions to this cold solution. The mixture turns dark purple as ferrate dianions, FeO₄²⁻, form, according to the following scheme:



Solid potassium hydroxide is added again to this purple solution, precipitating potassium ferrate(VI), which was then separated by vacuum filtration through a coarse glass filter. Black crystals thus produced were washed with few portions of cold hexane and diethyl ether to remove traces of water. The stability of the product crucially depends on water removal. It was kept in dessicator over KOH pellets. Barium ferrate was prepared in an essentially same way, except that commercial bleach (sodium hypochlorite solution) was applied instead of potassium hypochlorite.

Total iron in these preparations was determined by standard methods using absorption spectrum of Fe(II) - 1,10-phenanthroline complex, while iron(VI) was estimated by the reaction with an excess of chromium(III) nitrate in alkaline solution:



Chromate was converted into dichromate by acidification, and the latter titrated by a standard solution of ferrous sulfate with sodium diphenylamine sulfonate redox indicator (Schreyer and et al. 1951). The results were compared with the optical absorption of the product in its absorption peak of 510 nm, taking 11,500 M⁻¹cm⁻¹ for ferrate(VI) molar extinction (Carr et al. 1985). Nearly 90% purity was attained, according to these measurements, for potassium ferrate(VI).

2.2. Spectral Characterizations

UV-Visible absorption spectra of ferrate(VI) solutions in 10 M KOH were recorded using diode array spectrophotometer HP 8453.

Visible and IR reflectance spectra were measured on Beckman 5240 and Pima (Integrated Electronics) instruments.

X-band EPR spectra were recorded from potassium ferrate powder and solutions at 300 and 77K, using Bruker ESP-300E instrument operating at 100 kHz modulation frequency, and with microwave power below saturation.

Mössbauer spectra were obtained at 300K in zero magnetic field using a conventional constant acceleration spectrometer (Ranger Scientific) with 1024-channel pulse height analyzer and a Kr gas proportional counter. ^{57}Co in a rhodium matrix was used as a radiation source and isomer shifts are given with respect to metallic iron at 22°C. All spectra were measured in helium gas flow. Powdered samples were sandwiched between two Kel-F plastic holders (teflon-like material) and measured immediately. The Kel-F holders appear to be non-reactive with the Fe(VI) sample during the measurement as evidenced by the observation that after the sample and cell were removed from the spectrometer neither the sample nor the Kel-F cell shown any discoloration that might have indicated an alteration reaction with the Fe(VI) sample. However, after several days in contact with the Kel-F holder, severe discoloration and physical alteration of the holder were apparent.

Magnetic hysteresis loops (magnetization versus magnetic field) at room temperature and in fields up to 1.5 Tesla were measured using a vibrating sample magnetometer. About 100 mg of fresh sample was placed in a small plastic capsule and measured immediately. The time for a complete hysteresis measurement was 15 minutes.

X-Ray absorption near edge spectra (XANES) were obtained using the Material Research Collaborative Access Team Sector at the Advanced Photon Source, Argonne National Laboratory.

2.3 Studies of the Chemical Reactivity of Ferrate

Gases released in the reactions of ferrate(VI) with ordinary water and H_2^{18}O , and with aqueous solutions of organic compounds, were analyzed in two ways:

First, using Micro-Oxymax close-circuit respirometer (Columbus Instruments) designed to detect low levels of oxygen and/or carbon dioxide production/consumption. The volumes of gases are automatically

normalized to standard temperature and pressure, and may be also presented in $\mu\text{g}/\text{min}$.

Second, using Varian Saturn 2000 GC-MS instrument. The column used was a Supelco Carboxen 1010 PLOT capillary column, 0.32 mm i.d., 30 m length. The temperature program started with the temperature of 35°C held for 5 min, then increases to 150°C at 20°C/min. Helium was used as a gas, at a flow rate of 1.5 mL/min. The mass spectrometer collected data for a mass range of 10 to 100 amu.

Thermal decomposition of the material was studied by means of differential scanning calorimetry (Shimadzu DSC-50, 5 C/min heating rate, aluminum hermetically sealed sample holder) and thermal gravimetric analysis (Shimadzu TGA-50, 5 C/min heating rate, platinum sample holder, N₂ atmosphere), all in dry-box.

3. RESULTS AND DISCUSSION

Assessing the possible role of ferrate(VI) as an oxidant on the Mars surface, we address the following few questions:

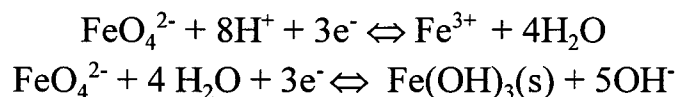
1. Is there an opportunity to form ferrate (VI) on Mars, according to what is presently known about its surface composition and environmental conditions?
2. Would such a compound be stable enough to persist and accumulate under those conditions?
3. Would it be able to display essential reactivity that was found in the samples of Martian soil in Viking experiments, i.e. to produce oxygen gas while moisturized, and
4. Would it produce carbon dioxide while contacting with organic materials that constituted nutrient solution in those experiments?
5. Would these chemical activities be impaired at heating in a way similar to such an inactivation in Viking's experiments?
6. Having in mind Mars exploration programs, what are the possible approaches for identification of ferrate(VI), and in particular what are the spectral features of this species that permit its characterization by both contact measurements and remote sensing?

3.1 On the Formation and Persistence of Ferrate(VI) in Martian Soils

Regular way to ferrate(VI) accepted as a synthetic approach in most relevant studies is that through wet oxidation of Fe(III) with hypochlorite, as

it was applied in these experiments. However, formation of ferrate(VI) was found in the reactions of iron-containing materials with some peroxides (Kopelev *et al.* 1992, Dedushenko *et al.* 1997). On the other hand, there is a strong belief that active oxygen species, peroxides, superoxides, hydroxyl radicals and possibly ozone can form under UV irradiation in Martian atmosphere, and affect its soil [Bullock, *et al.* 1994, Huguenin, *et al.* 1979, Hunten, D. 1979, McDonald, *et al.*, 1998]. Overall, Martian atmosphere is highly oxidized, with domination of carbon dioxide and presence of some dioxygen. In these circumstances, ferrate(VI) can serve as a form of stabilization and storage of active oxygen, if however its decomposition is slow enough to permit its accumulation.

Ferrate(VI) is rather stable in strongly alkaline solutions only, at pH>10, and even in these solutions it is readily reduced by most of organic materials. In pH-E° diagram, where E° is oxidation potential of the system, the stability region can be approximately presented as shown in fig.1. In constructing this diagram, by extending that published earlier by Stumm and Morgan (1970), it was taken into account that the reduction potentials for the Fe(VI)/Fe(III) couple have been estimated as 2.20 and 0.72 V versus NHE in acidic and basic solutions, respectively (Wood, 1958), according to the following equilibria:



At lower pH, not only organic materials, but water is oxidized, too. So, thermodynamically, one would need a highly alkaline environment for ferrate(VI) to be stored. This requirement is not so limiting for Mars soil, as it could seem on the first glance. Indeed, there are strong reasons to assume that in the absence of calcium carbonate biogenic deposits which now serve as a powerful buffer on Earth surface, both pre-Cambrian Earth and Mars at some stage of its geological history were covered with “soda ocean” with pH>9 (Kempe and Degens 1985, Mills and Sims 1995).

Ferrates of alkaline metals are rather unstable in the presence of moisture. However Martian surface is extremely dry and cold. Thus, even alkaline ferrates can be stabilized there. Besides, other ferrates, such as BaFeO₄, are much less water soluble and at the same time more stable in humid milieu. Essential is that ferrate(VI) is not sensitive to light (Wagner *et al.* 1952).

Therefore, there is enough reason to suggest that the formation of ferrate (VI) and its preservation in soil are consistent with present knowledge of the chemical composition and environmental conditions at the Martian surface.

3.2. Spectral Characterization of Ferrate(VI)

3.2.1. Absorption and reflectance spectra

Deep purple color appearing in iron-containing highly alkaline solutions when treated with strong oxidants was found centuries ago. This characteristic color is due to the tetrahedral ferrate(VI) dianion, FeO_4^{2-} , with its absorption peak at 507-510 nm, as shown in fig. 2, and molar extinction of 1100-1300 $\text{M}^{-1}\text{cm}^{-1}$ at this wavelength. This spectrum makes ferrate(VI) very distinct from other forms of dissolved iron, and makes absorption spectrum an appropriate tool for ferrate(VI) identification and quantitation when samples are available for dissolution.

With Mars exploration in view, more practical seem reflectance spectra that can be recorded by remote sensing from orbit. Broad range reflectance spectrum of crystalline potassium ferrate is presented in fig.3, together with other forms of iron, and their mixtures. The band at 1.6 μm is a characteristic one, and it can be used as a marker to search for the presence of Fe(VI) on the Martian surface. Reflectance spectra in a more narrow visible range are also included in fig. 3. They show general correspondence with the absorption spectra in fig. 2, and are also quite distinct from other forms of iron.

3.2.2. Mössbauer Spectra and Magnetic Measurements

Mössbauer spectroscopy is probably the most powerful and straightforward approach to the identification of various oxidation states of iron. It is especially important in the context of these studies since a compact Mössbauer instrument has been developed for the future Mars missions and will be a part of Athena payload (Klingelhöfer *et al.* 1996, Klingelhöfer 1999). The room temperature Mössbauer spectrum of a sample containing potassium ferrate(VI), together with other iron species, is shown in fig. 4, together with a diagram of the ranges of isomer shifts in iron compounds with various valences and spin states, as referenced to iron metal at 300K. . It is produced by a superposition of two main spectral components. One component consists of a singlet line with a negative isomer

shift of -0.91 mm/s, and the other is a quadrupole-split doublet with an isomer shift of +0.32 mm/s and quadrupole splitting of 0.57 mm/s. The relative abundance of these two components were estimated from the relative area of the two sub-spectra and indicated that the singlet component accounted for 48% of the total area.

The singlet component has a negative isomer shift, which is opposite in sign to the isomer shifts for Fe(II) and Fe(III) phases. This component is identified as the primary Fe(VI) phase and its isomer shift is slightly more negative than previously reported for this compound (Wertheim and Herber, 1962). A negligible quadrupole splitting is expected for Fe(VI) in K_2FeO_4 based on its $3d^2$ electronic configuration in a tetrahedrally coordinated site. The doublet component has an isomer shift and quadrupole splitting consistent with an Fe(III)-bearing phase which is paramagnetic at room temperature.

In addition to the two main components, a barely discernible magnetically split sextet was also observed (fig. 4) with a magnetic hyperfine field of 49.7 T. The full sextet hyperfine spectrum is observed in magnetically ordered materials when the atomic magnetic moments are fixed in space for a time greater than 10^{-9} s. The presence of a magnetically ordered phase was also confirmed from the room temperature magnetization measurements. At room temperature, the field-dependent magnetization approaches saturation but shows no hysteresis, typical of superparamagnetic behavior exhibited by nanophase iron-oxide magnetic materials (grain size <30 nm). From the bulk value of saturation magnetization ($M_s=0.325$ Am²/kg), the iron-oxide phase is most likely a strongly magnetic phase such as magnetite ($M_s=92$ Am²/kg) or maghemite ($M_s=75$ Am²/kg) rather than a weakly magnetic phase such as hematite ($M_s=0.4$ Am²/kg) or an iron oxyhydroxide phase. Otherwise, the hematite/Fe-oxyhydroxide phase would be over 90% of the sample by weight and would readily be detected with Mössbauer. Assuming the phase is magnetite or maghemite, the bulk M_s value indicates that this phase is about 0.4% by weight consistent with the weak sextet sub spectra observed in fig. 4. It also showed that Mössbauer spectrum of Fe(VI) can be easily detected in the presence of iron in other oxidative states.

3.2.3. EPR Spectra

Ferrate(VI), with its sd^3 hybridized iron, and $3d^2$ electron configuration, is paramagnetic and EPR active. Electron paramagnetic resonance spectra of magnetically diluted oriented single crystals of several salts of general formula K_2MO_4 ($M = S, Cr, Se$), isomorphously doped with FeO_4^{2-} anions, have been previously published and theoretically analyzed in full detail (Abdulsabirov *et al.* 1979, Wagner *et al.* 1995). Non-oriented powder samples display a singlet EPR spectrum at $g \approx 1.9948$, with line-width of *ca.* 8 mT at 77 K, which is significantly broadened at room temperature (fig. 5). This, again, opens an opportunity of searching for Fe(VI) in future Mars missions, since the development of a miniaturized EPR instrument is underway (Kim, *et al.* 1997).

3.2.4. X-Ray Spectra

XANES spectra of ferrate(VI) sample are shown in the fig. 6. In this technique, the focus is on the region very close (within about 30 eV) to the ionization threshold of the compound in question. The structure of the absorption spectrum in this region is very sensitive to the three-dimensional geometry of the atoms surrounding the excited atom (iron atom in these studies). Comparison of XANES spectra of a sample with XANES spectra of known standards allows identification of the oxidation state and local geometry around iron. For iron, X-ray absorption edge energy is ~ 7112 eV, and characteristic pre-edge feature is observed from both solutions and solid samples containing tetrahedrally coordinated Fe(VI) in ferrate dianion. Additionally, more subtle changes in X-ray absorption edge energy have been shown to enable the identification of Fe(II) and Fe(III) valence states (a more detailed discussion of the XAS data collection, analysis, and interpretation submitted to the Journal of Synchrotron Radiation).

3.3. Chemical Reactivity of Ferrate(VI)

3.3.1. Thermal Decomposition

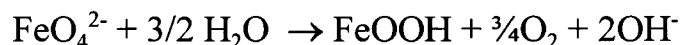
In the Viking Gas Exchange Experiments, it was found that samples of Martian soil released oxygen in the amounts of 70 to 700 nmol / μ L upon introduction of water into the sample cell (Oyama *et al.*, 1976, Levin and Straat, 1977). Oxygen was released also from a sample of soil that had been pre-heated at 145°C, even though the amount of gas was substantially reduced.

Potassium ferrate(VI) as a dry powder is stable at room temperature. However, at heating it decomposes releasing dioxygen. This decomposition slowly proceeds starting about 50°C and is complete by 300°C. Thermal decomposition is a complex, multi-stage process, as can be seen from thermogram and DSC observations (fig. 7). One may speculate that lower oxidation states of iron, such as Fe(+5) and Fe(+4) are first produced, before the final product, Fe₂O₃, forms. Catalytic effect of Fe(III) on ferrates decomposition is anticipated and may significantly complicate the results of DSC and thermogravimetry analysis.

3.3.2. Water Oxidation

Dry ferrate is not immediately reactive with such aprotic solvents as ether, chloroform, benzene, which permits their application for removal of traces of water from ferrate preparation at the final stage of its purification. Neither is ferrate(VI) soluble in any of those solvents. Though methanol has also been recommended in some publications for water removal, in our hands, its application invariably resulted in partial reduction of ferrate(VI) to iron(III).

Upon addition of water to potassium ferrate (VI), the mixture bubbles indicating an intensive gas evolution. GC-MS analysis of gas product after reaction of potassium ferrate with H₂¹⁸O revealed that the gas product formed in the head space of reactor vessel is ¹⁸O₂ (data not shown), in accordance with results published earlier which indicated a little ferrate-water exchange of oxygen, which is enhanced by acids (Goff and Murmann 1971). Hence, reaction consists in true water oxidation:



Barium ferrate(VI) was much less reactive under comparable conditions, along with its low solubility.

The kinetics of dioxygen accumulation at the reaction of potassium ferrate with water is shown in fig. 8.

Preheating of potassium ferrate(VI) samples up to 160°C resulted in partial decomposition of the stuff, which then produced a smaller amount of oxygen when moisturized.

3.3.3. Generation of Carbon Dioxide from Organic Material

In the Viking Labeled Release Experiment (Levin and Straat 1976), $^{14}\text{CO}_2$ was rapidly released upon contact of the surface material with ^{14}C labeled nutrient solution. The reaction slowed down after a small fraction of the added organic medium decomposed. Preheating the samples up to 160°C for three hours completely inhibited the release of $^{14}\text{CO}_2$ (Levin and Straat, 1977).

According to their respective redox potentials, ferrate(VI) is a stronger oxidant than permanganate and chromate.

Table 1. Standard potentials, E° , *volt*, of few redox couples in acidic and alkaline solutions

acidic solution		alkaline solution	
$\text{FeO}_4^{2-}/\text{Fe}^{3+}$	2.20	$\text{FeO}_4^{2-}/\text{Fe}(\text{OH})_3(\text{s})$	0.78
$\text{MnO}_4^-/\text{MnO}_2$	1.68	$\text{MnO}_4^-/\text{MnO}_2(\text{s})$	0.59
$\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$	1.33	$\text{CrO}_4^{2-}/\text{Cr}(\text{OH})_3(\text{s})$	- 0.12

Extremely strong oxidizing power of ferrate(VI) was well documented in its reactions with a number of various compounds: it converts chromium(III) to chromate (Schreyer *et al.* 1951), oxidizes ammonia, cyanide (Sharma *et al.* 1998a, b), hydrogen sulfide and other sulfur compounds (Johnson and Read, 1996, Sharma *et al.* 1997, Read *et al.* 1998, Read and Wyand, 1998), and was proposed as a valuable oxidizing reagent for organic synthesis (Delaude and Laszlo 1996, Norcross *et al.* 1997) and wastewater treatment (Carr, *et al.* 1985).

In our experiments, addition of aqueous solutions of formate and/or lactate to powdered potassium ferrate(VI) resulted in the release of carbon dioxide in head space of the reactor vessel, due to the oxidation of organic carbon. At the same time, some dioxygen was also formed, apparently due to a concomitant reaction with water. Preheating ferrate at 105°C for 4 hours considerably inhibited CO_2 evolution. The inhibition increased at 160° (fig. 9). These observations are in line with the results of Viking Labeled Release Experiments.

The relative yield of both gases is a complex function of the final pH of the solution formed at the addition of aqueous organic substrate to ferrate, i.e. of the amount of the solution, substrate concentration, buffer capacity, and the amount of solid ferrate taken. In an experiment where both gases were measured simultaneously, the pH dependence was obtained as shown in the Fig. 10.

All in all, the analysis of the data available shows that iron in its higher oxidation state can be considered a plausible candidate for a part of oxidative pool in Martian soil. This hypothesis is verifiable, and there are good prospects to test it in forthcoming Mars missions, through measurements by both remote sensing and contact experiments *in situ*, and by the analysis of the returned samples.

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Captions

Fig. 1. Approximate pH-E° diagram of most abundant iron compounds. Ferrate(VI) occupies the upper-right part of the diagram.

Fig. 2. Visible absorption spectra of iron compounds in solutions. 1-K₂FeO₄, 1.7·10⁻⁴M, in 10 M KOH. Characteristic peak at 507 nm, $\epsilon_{507}=11000 \text{ M}^{-1}\text{cm}^{-1}$. 2 - Same solution after reduction with acetone; 3-0.1 M FeSO₄, pH 4.5; 4-0.1Fe₂(SO₄)₃, pH 4.5.

Fig. 3. Reflectance spectra of iron compounds. 1- Broad range spectrum of solid potassium ferrate; 2-7: spectra in the range 1200-2400 nm. 2 - Solid K₂FeO₄; 3 - Fresh precipitate of FeOOH; 4 - CaO-Fe₂O₃ mixture; 5 - CaO-Fe₂O₃-K₂FeO₄ mixture; 6 - Solid FeSO₄; 7 - Solid Fe₂(SO₄)₃. 8 - 9: Visible range reflectance spectra. 8 - CaO - Na₂FeO₄ mixture; 9 - Al₂O₃-Fe₂O₃ mixture.

Fig. 4. Mössbauer spectrum of ferrate(VI) - Fe₂O₃ mixture, and the diagram (Fultz, 1997) of typical isomer shifts for iron compounds with various valences and spin states, with reference to αFe at 300K.

Fig. 5. EPR spectra of powdered ferrate (VI) at 77 K and room temperature.

Fig. 6. XANES spectrum of ferrate(VI).

Fig. 7. Thermal decomposition of potassium ferrate(VI) samples: thermogravimetry (a) and DSC (b) results.

Fig. 8. Accumulation of oxygen at the reaction of potassium ferrate(VI) with water.

Fig. 9. Release of carbon dioxide at the reaction of potassium ferrate(VI) with aqueous format, 0.1 M. Effect of preheating of ferrate

Fig. 10. Effect of pH of the formate solution on the amount of oxygen and carbon dioxide released in the reaction with ferrate (simultaneous measurements).

E° –pH Diagram for Iron Compounds

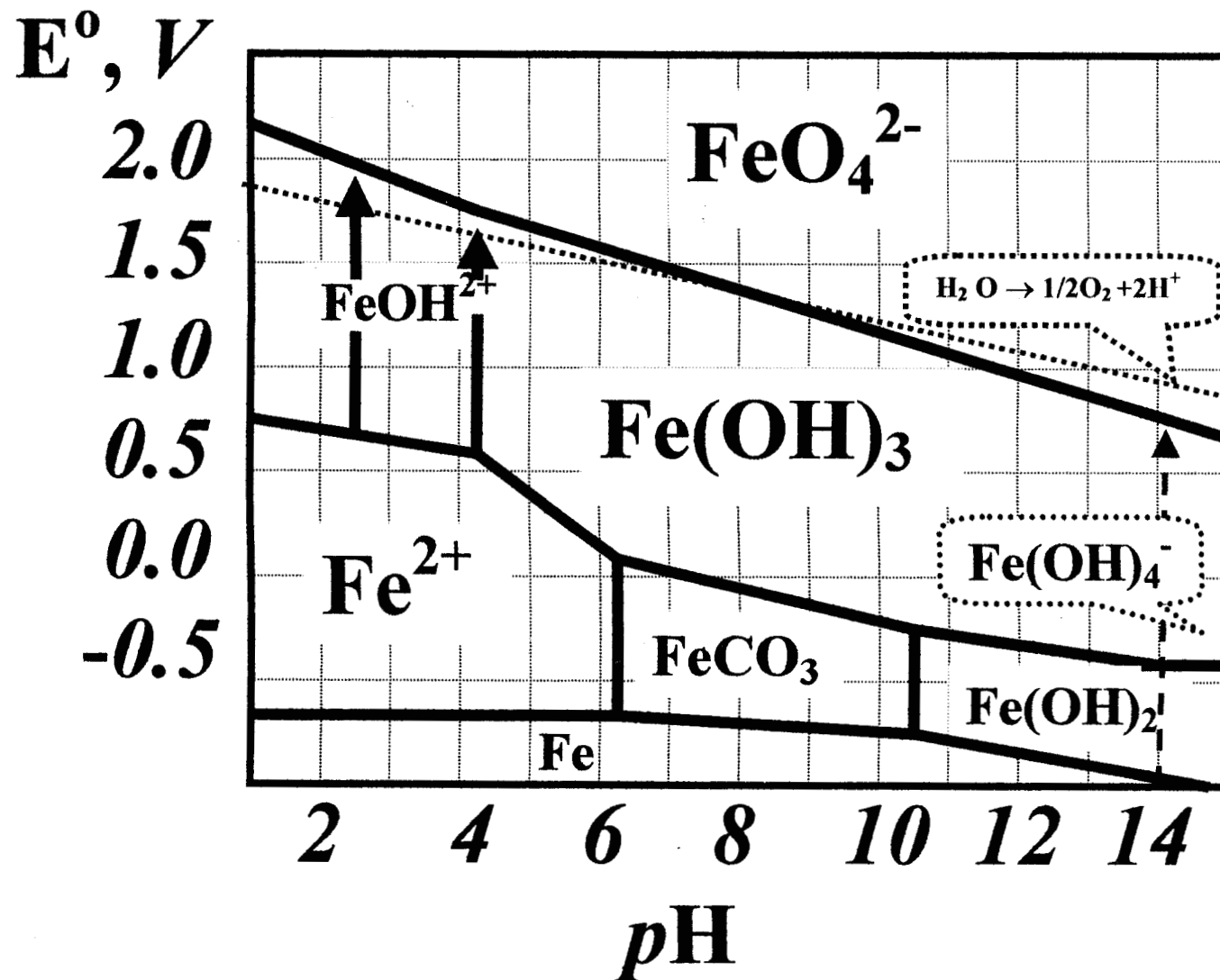


Fig 1. Teyssie et al.

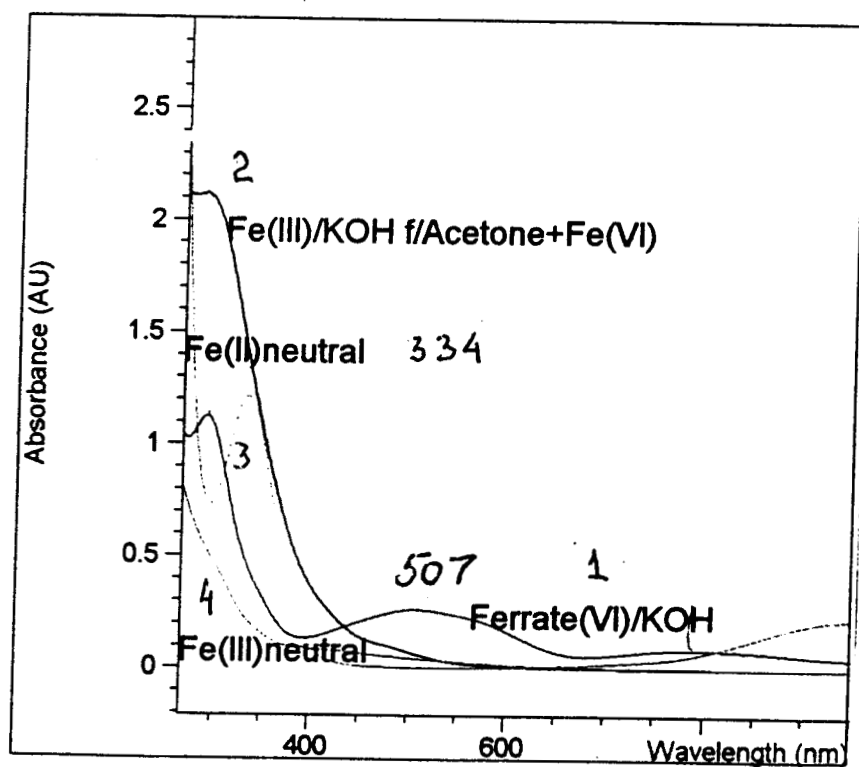


Fig 2 Tbarin et al.

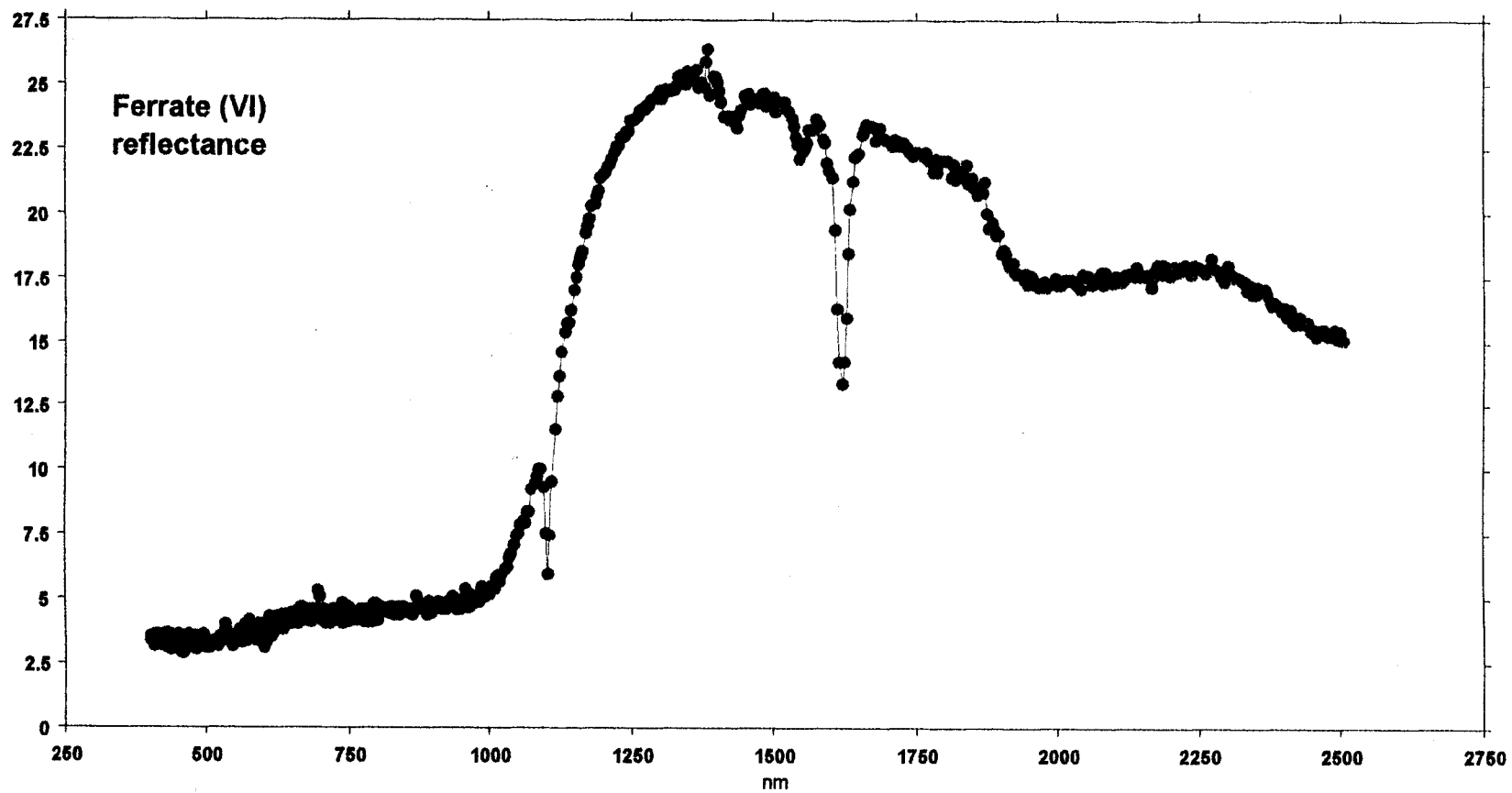


Fig 3 : 1

Tsopila et al

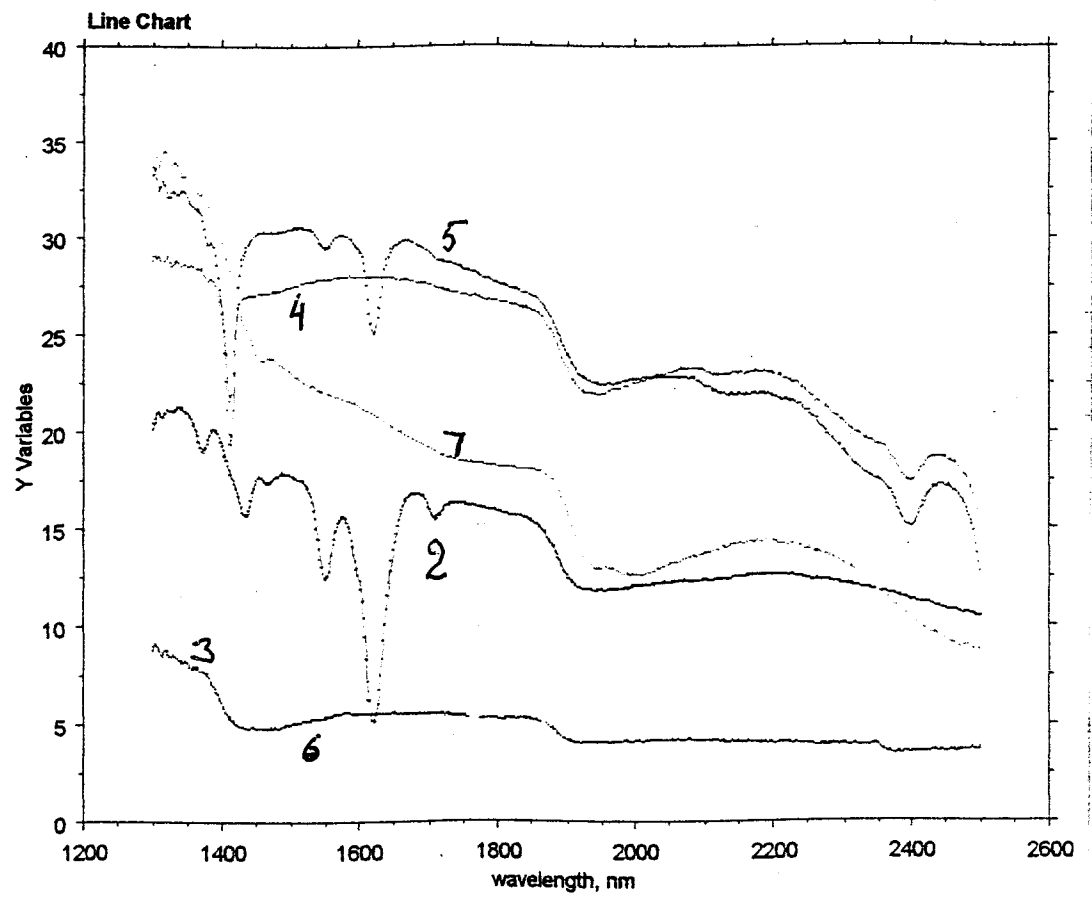
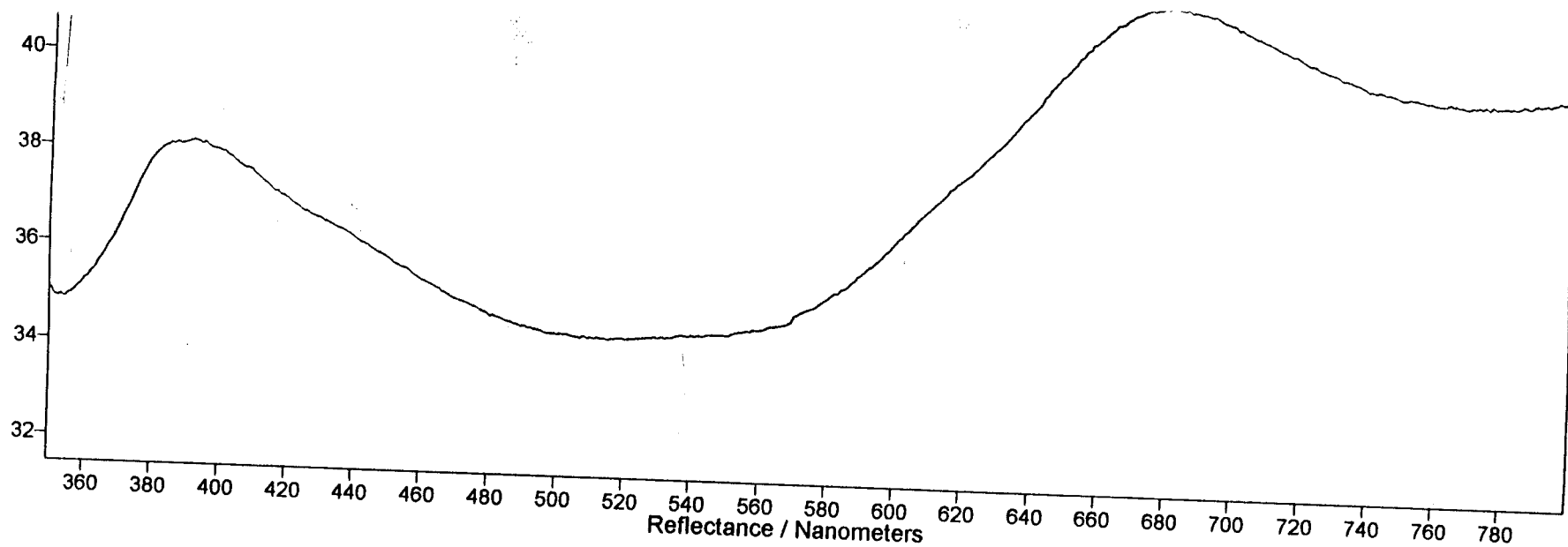


Fig. 3: 2 to 7

Fig 3.

8



9

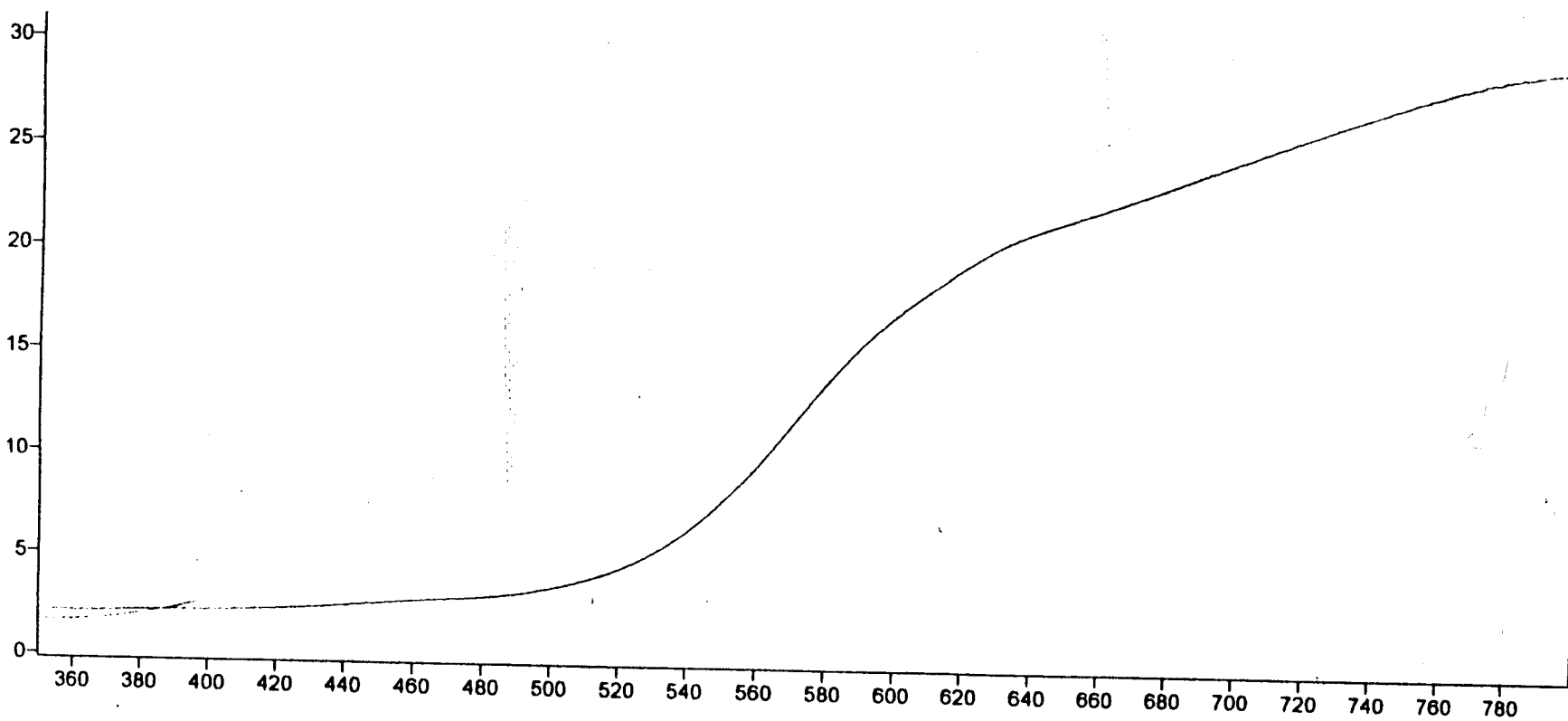


Fig 4.

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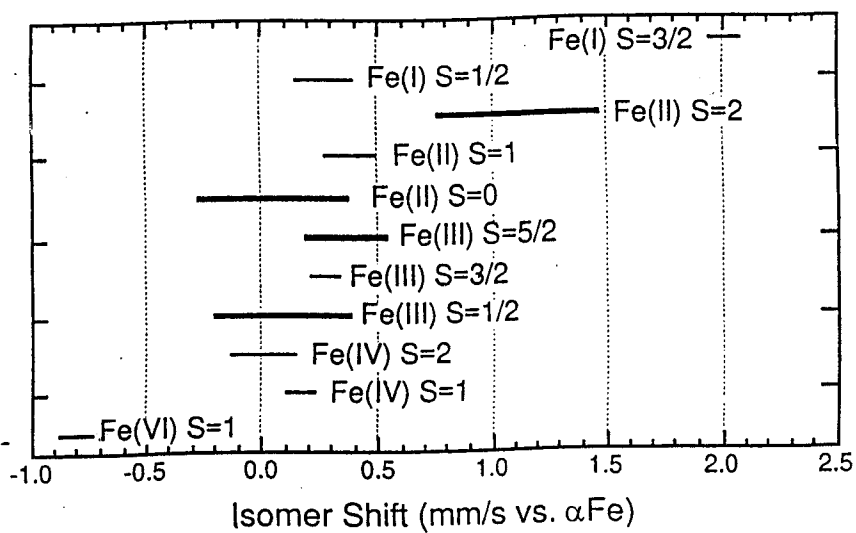
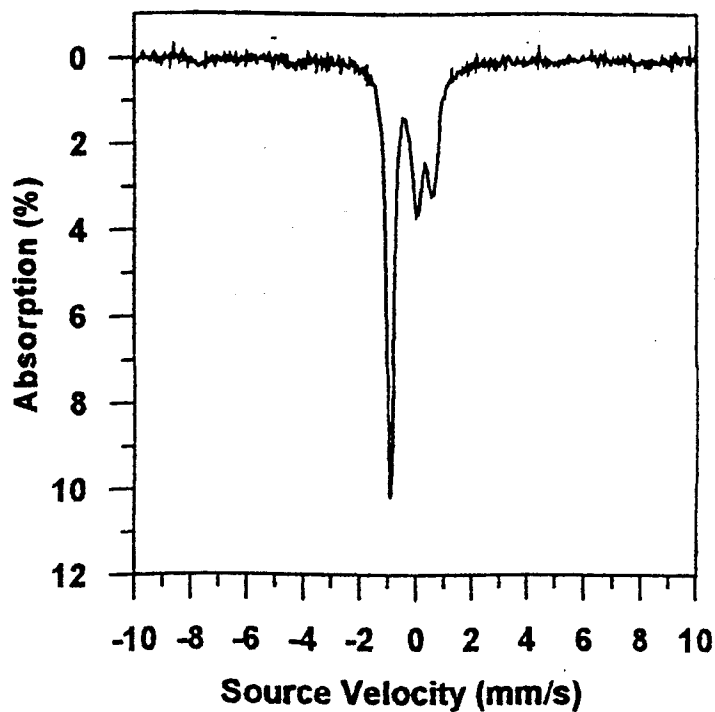


Fig 5

Tsagin et al

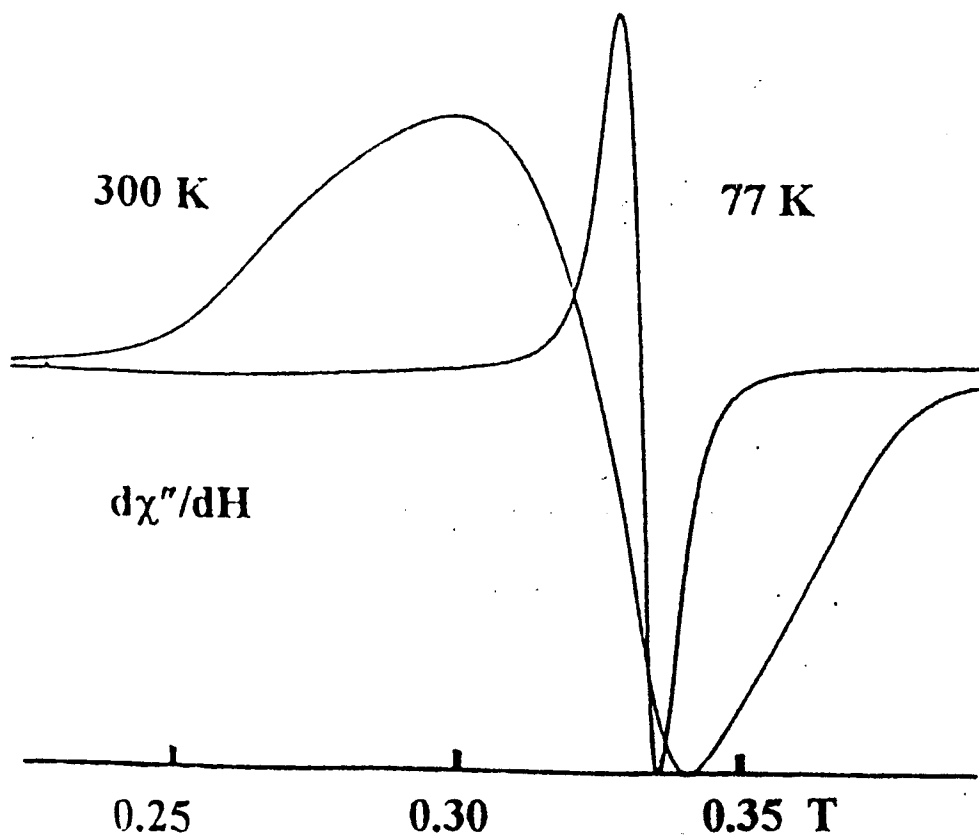


Fig 6. Teyen et al.

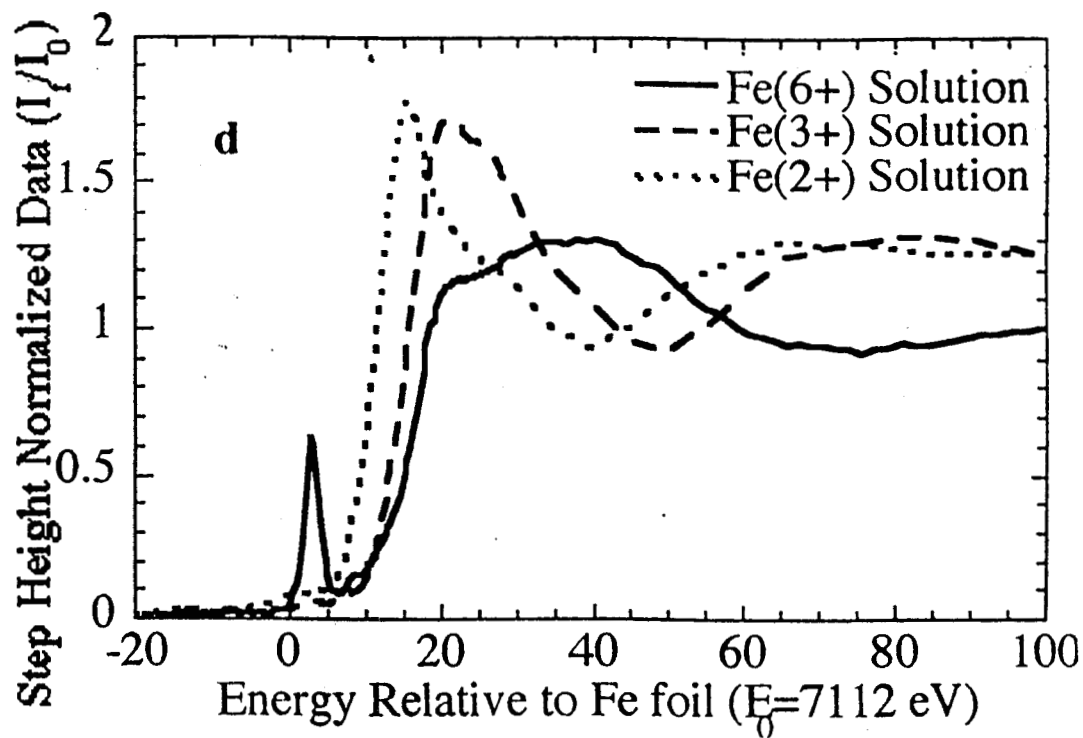
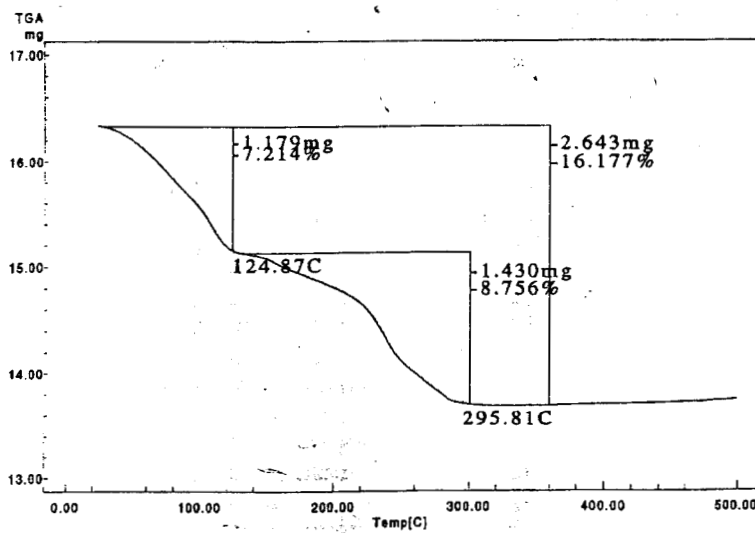


Fig. 7.

a



b

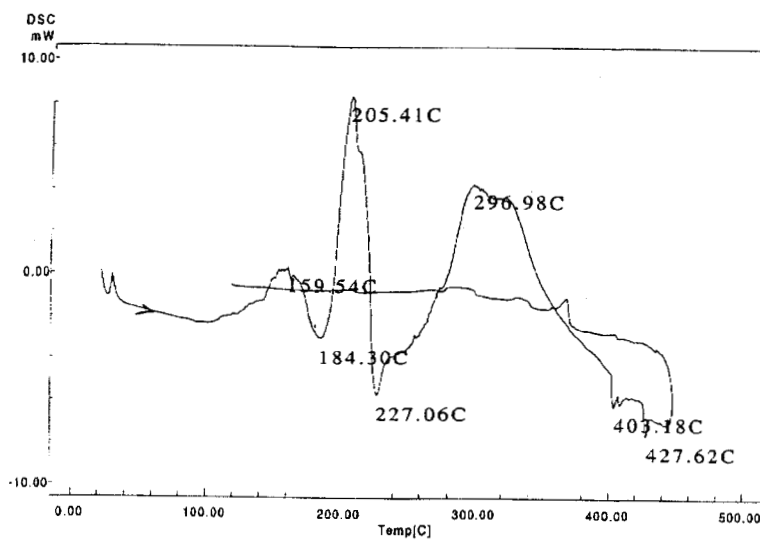


Fig. 8.

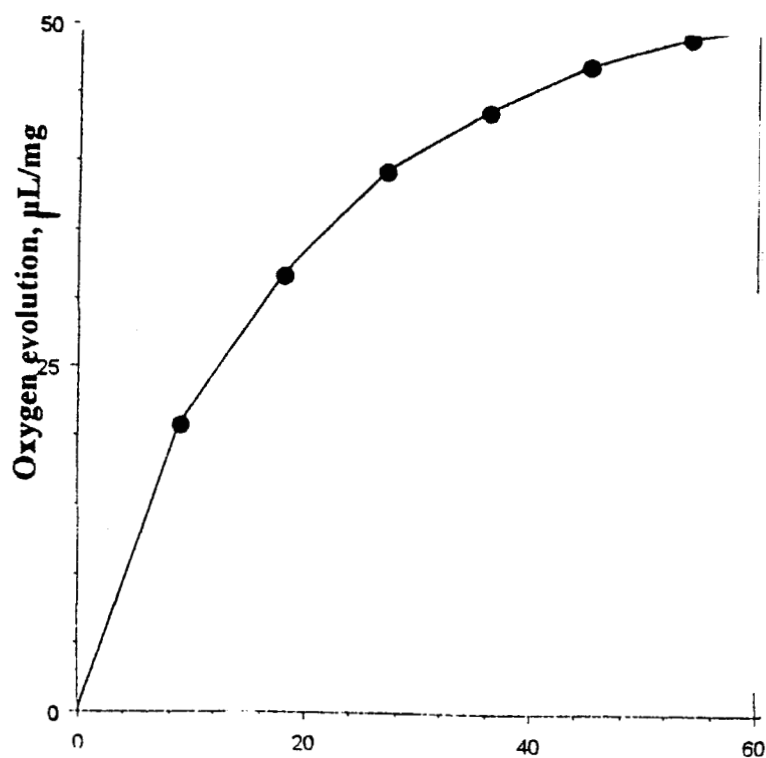


Fig 9. Tbspin et al.

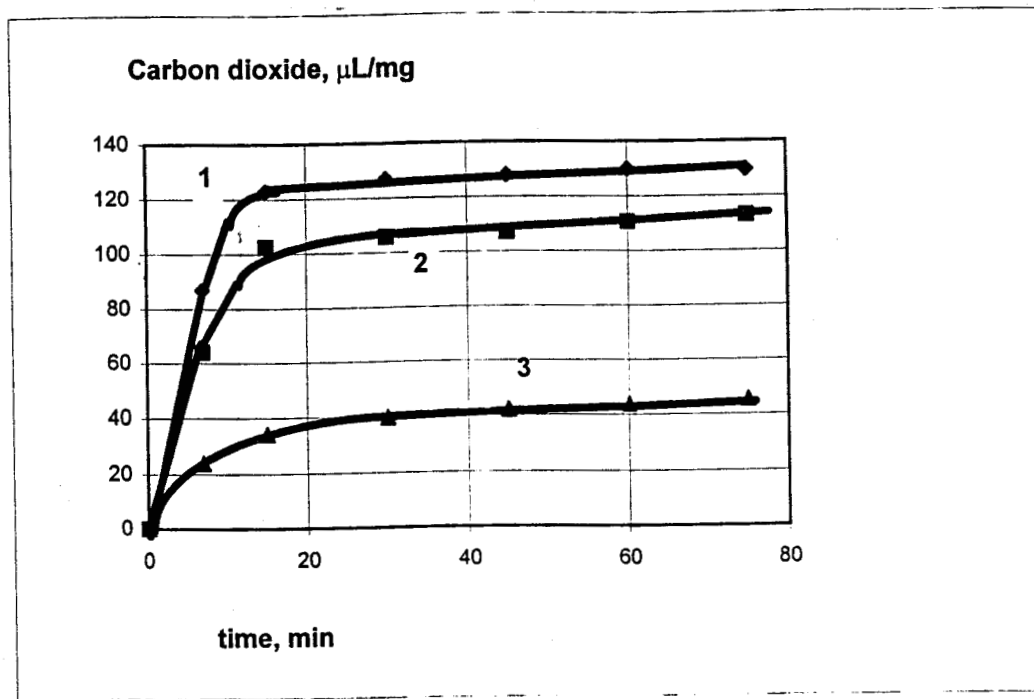


Fig 10. Dey et al

